

PATENT ABSTRACTS OF JAPAN

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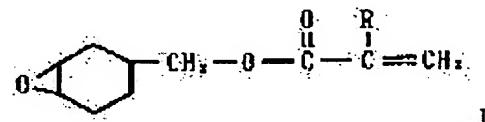
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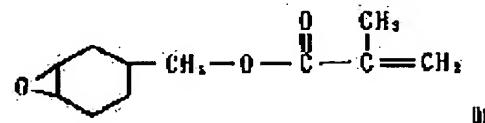
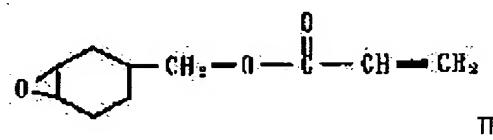
(54) PHOTOCURABLE OLIGOMER, RESIN COMPOSITION CONTAINING SAME, AND ITS CURED ARTICLE

(57)Abstract:

PURPOSE: To obtain a photocurable oligomer which gives a printing ink excellent in gloss, pigment dispersion, printability, etc., by reacting a specific compd. with rosin.



CONSTITUTION: A photocurable oligomer is prep'd. by reacting a compd. of formula I (wherein R is H or CH₃) (e.g. a compd. of formula II or III) with rosin. The type of rosin used is determined considering the rate of ultraviolet curing of the resulting ink, the hue of the oligomer, etc., and usually rosins with conjugated double bonds stabilized, such as a hydrogenated rosin or a disproportionated rosin, are suitable. The oligomer can be used for various applications by utilizing its photocurability and gives, when used as a binder, a printing ink excellent in gloss, pigment dispersion, printability, etc., in comparison with conventional solvent-based printing inks.



LEGAL STATUS

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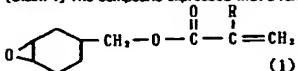
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CLAIMS

[Claim(s)]

[Claim 1] The compound expressed with a formula (1) [** 1]



(— R is H or CH₃ among a formula.) -- photoresist oligomer which is a reactant with rosin.

[Claim 2] The resin constituent characterized by containing photoresist oligomer according to claim 1.

[Claim 3] The hardened material of a resin constituent according to claim 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to new photoresist oligomer, the resin constituent using this, and its hardened material. In more detail, it is the oligomer which has ultraviolet-rays hardenability, and is related with the resin constituent and hardened material using the photoresist oligomer and this suitable for especially the binder for printing ink.

[0002]

[Description of the Prior Art] The ultraviolet curing ink is known as a constituent which blends suitably reactant diluents, such as trimethylolpropane triacrylate, a photopolymerization initiator, a pigment, etc. with the partial saturation epoxy resin ester usually reacted and obtained in an epoxy resin and an acrylic acid, and is obtained. In this, although partial saturation epoxy resin ester, unsaturated polyester, etc. are positioned as oligomer in the binder for ink, since this oligomer relates to many ink properties acquired [cure rate / gloss, pigment dispersibility, viscosity, a printability,] closely, it is important also especially in said constituent.

[0003]

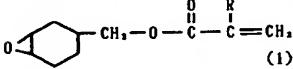
[Problem(s) to be Solved by the Invention] In recent years, even if it is an ultraviolet curing ink, it is required that it should have a printability comparable as conventional solvent mold ink, and it is in the situation that it cannot be satisfied with the partial saturation epoxy resin which is conventional polyfunctional oligomer of this demand enough.

[0004] For example, as a partial saturation epoxy resin, although the reactant of the epoxy resin of bisphenol A and an acrylic acid (meta) is known, when an ultraviolet curing ink is prepared using this, there is a fault that emulsification and the misting phenomenon of ink are especially accepted notably among printabilities. Therefore, development of the new oligomer which can offer the ultraviolet-rays hardenability ink which has the outstanding printability is demanded.

[0005]

[Means for Solving the Problem] With the conventional technique, this invention is made in order to be able to solve and to solve the inside **** aforementioned technical problem, the invention persons found out that said technical problem could be solved by using the specific oligomer which has a resin component in a side chain, as a result of repeating research wholeheartedly that the outstanding photoresist oligomer with which can be satisfied of these many engine performance should be developed in consideration of a cure rate besides a printability, stability on board, etc. That is, this invention is a compound [0006] expressed with 1. type (1).

[Formula 2]

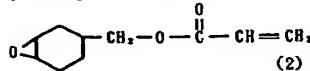


[0007] (— they are the inside R and H of a formula, or CH3) — it is related with the hardened material of the resin constituent characterized by containing the photoresist oligomer and the photoresist oligomer given in 2. 1st term which are a reactant with rosin, and a resin constituent

given in 3. 2nd term.

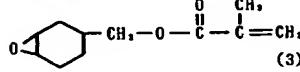
[0008] The new photoresist oligomer of this invention can be obtained by making the compound and rosin which are expressed with said formula (1) react. As an example of a compound expressed with a formula (1), it is [0009].

[Formula 3]



[0010]

[Formula 4]



[0011] — things are made. The rosin which was determined in consideration of the ultraviolet-rays cure rate of the ink obtained, the color tone of photoresist oligomer, etc., and usually carried out stabilizing treatment of the conjugated double bond, such as hydrogenation rosin and disproportionation rosin, is suitable for rosin. For example, the product made from Arakawa Chemical industry, a trade name, HAPE-RU (hydrogenation rosin), KR-610 (colorless rosin), etc. can be mentioned.

[0012] The reaction of the compound and rosin which are expressed with a formula (1) performs preferably about 0.9~1.1Eq of compounds expressed with a formula (1) to 1Eq of the carboxyl group of rosin by the ratio which becomes about 0.95~1.1Eq preferably especially. In order to promote a reaction, it is desirable to use catalysts (for example, triethylamine, benzyl dimethylamine, methyl triethyl ammoniumchloride, triphenylphosphine, etc.), and the amount of this catalyst used is 0.3~5 % of the weight especially preferably 0.1 to 10 % of the weight preferably to reaction raw material mixture. In order to prevent the polymerization under reaction, it is desirable to use polymerization inhibitors (for example, METOKINON, hydroquinone, phenothiazin, etc.), and the amount used is 0.05~0.5 % of the weight especially preferably 0.01 to 1 % of the weight preferably to reaction raw material mixture. 60~150 degrees C of reaction temperature are 80~120 degrees C especially preferably preferably. Moreover, reaction time is 10~50 hours especially preferably preferably for 5 to 60 hours.

[0013] Since hyperviscosity [the resin constituent of this invention / photoresist oligomer], it usually uses a reactant diluent in the range of the 20~700 weight section to the photoresist oligomer 100 weight section of this invention if needed for the purpose of a viscosity drop. As this reactant diluent, 2-hydroxyethyl (meta) acrylate, Tripropylene glycol di(methyl)acrylate, hydroxylate neopentyl glycol di(methyl)acrylate, Bisphenol A tetra-ETOKISHIJI (meta) acrylate, bisphenol F tetra-ETOKISHIJI (meta) acrylate, Trimethylol propane TORI (meta) acrylate, trimethylol propane TORIPUROPOKISHITORI (meta) acrylate, Dimethylol propane tetrapod (meta) acrylate, tricyclododecane dimethyl di(methyl)acrylate, dipentaerythritol hexa, PENTA (meta) acrylate, etc. can be mentioned. these reactivity diluent — one sort — or two or more sorts can be used.

[0014] When using the resin constituent of this invention as printing and a binder for ink, pigments, such as fast erucism-, benzidine erucism-, Lake Red 4R, Lake Red C, brilliant carmine 6B, a copper phthalocyanine blue, a titanium white, and carbon black, can usually be further distributed and used at 50 or less % of the weight among the resin constituent of this invention if needed. Furthermore, extenders, such as an alumina and silicon, may be distributed and used. moreover, in case [like ultraviolet rays] the activity energy line of low energy is comparatively used as a hardening energy line A benzophenone, a thioxan ton, benzoin ethyl ether, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholinopropane-1-ON, A diethoxy

acetophenone, 2-hydroxy - Photopolymerization initiators, such as 2-methyl-1-phenyl propane-1-ON, usually among a resin constituent 0.5~20 % of the weight. It is desirable to use aliphatic series, aromatic amine or 4, and 4-screw diethylamino benzophenone etc. as an accelerator 0.1 to 10 % of the weight among a resin constituent if needed furthermore.

[0015] Furthermore, a part of epoxy (meta) acrylate known from the former other than the photoresist oligomer of this invention, urethane (meta) acrylate, etc. can also be used together as a resin constituent of this invention. By adding said reaction diluent etc. further and hyperviscosity-izing, further, etc., the resin constituent of this invention can be used as a coating, adhesives, a solder resist, an overprint varnish, etc. and can also be further used as a charge of moldings lumber. The resin constituent of this invention can be obtained by mixing each component to homogeneity. The hardened material of the resin constituent of this invention can be obtained by irradiating ultraviolet rays or an electron ray with a conventional method, and making it harder.

[0016]

[Example] An example explains this invention to a detail further below. The section shows the weight section among an example.

The example 1 colorlessness rosin (product [made from Arakawa Chemical industry], KR-610, disproportionation rosin, acid number 170 (mgKOH/g) 200 section, the compound 115 section of said formula (2), the methyl triethyl ammoniumchloride 1.14 section, and the METOKINON 0.3 section are taught, temperature up is carried out to 95 degrees C, and it reacts at 95 degrees C. It reacted until the acid number (mgKOH/g) of reaction mixed liquor became five or less (about 25 hours), and the photoresist oligomer (product A) of this invention was obtained. The obtained product A was light yellow transparency in solid form in ordinary temperature. The result of having measured according to the high-resolution nuclear magnetic resonance (NMR) of the obtained product is shown below.

[0017]

No. PPM No. PPM 1 166.220 9 124.251 2 166.160 10 124.032 3 146.713 11 77.484 4 145.733 12 77.061 5 [130.712] 13 76.636 6 128.419 14 72.913 7 128.310 15 72.832 8 127.001 16 71.989 No. PPM No. PPM 17 71.707 45 38.872 18 71.662 46 36.741 19 68.352 47 36.695 20 68.181 48 36.555 21 68.040 49 36.348 22 67.493 50 36.243 23 67.274 51 35.390 24 67.22552 34.434 25 67.138 53 33.454 26 67.07054 33.333 27 67.028 55 33.092 28 56.260 56 32.808 29 49.989 57 32.610 33 47.785 58 32.125 31 47.713 59 32.02132 46.521 60 31.833 33 45.114 61 31.790 34 44.224 62 31.738 35 43.661 63 30.80036 40 462 6430.724 37 40.379 65 30.355 3838.423 66 29.832 3938.228 67 28.785 40 38.137 68 28.709 41 37.97069 28.635 4237.16770 27.834 43 37.053

| No. | PPM |
|-----|-----------|
| 7.3 | 2.5. 3.96 |
| 7.4 | 2.4. 8.12 |
| 7.5 | 2.4. 6.25 |
| 7.6 | 2.4. 4.26 |
| 7.7 | 2.3. 9.66 |
| 7.8 | 2.3. 9.02 |
| 7.9 | 2.2. 7.48 |
| 8.0 | 2.1. 8.23 |
| 8.1 | 2.1. 7.08 |
| 8.2 | 2.1. 6.22 |
| 8.3 | 2.1. 3.69 |
| 8.4 | 2.1. 3.02 |
| 8.5 | 1.9. 8.26 |
| 8.6 | 1.9. 7.74 |
| 8.7 | 1.9. 5.94 |
| 8.8 | 1.9. 3.12 |
| 8.9 | 1.9. 0.46 |
| 9.0 | 1.8. 6.27 |
| 9.1 | 1.8. 1.92 |
| 9.2 | 1.8. 0.90 |
| 9.3 | 1.6. 8.28 |
| 9.4 | 1.6. 5.87 |
| 9.5 | 1.4. 6.35 |
| 9.6 | 1.4. 5.22 |
| 9.7 | 0 |

71.27.131.44 37.014 72.26.087

[0018] In addition, the solvent performed the above-mentioned measurement by the proton decoupling method using heavy chloroform, using a tetramethylsilane as a reference material. [0019] The example 2 colorlessness rosin (product [made from Arakawa Chemical industry], KR-610, disproportionation rosin, acid number 170 (mgKOH/g) 200 section, the compound 124 section of said formula (3), the triphenyl phosphine 1.16 section, and the METOKINON 0.32 section were taught, it reacted at 95 degrees C (about 25 hours), and the photoresist oligomer (product B) of this invention was obtained. In ordinary temperature, Product B was a solid-state and was light yellow transparency.

N. Measurement result of M.R. [0020]

No. PPM No. PPM 1 178.358 20 77.054 2 178.000 21 78.631 3 187.483 22 72.950 4 167.418 23 72.874 5 187.369 24 72.498 6 146.706 25 71.9967145.747 26 71.901 8 137.499 27 71.7339138.58 28 68.428 10138.324 29 68.215116.26838.508 31 87.526 13 127.018 32 67.3424 125.944 33 67.27815 125.613 34 67.216 15 125.473 35 67.13817 124.269 36 58.843 18 124.032 37 58.300 19 77.477 38 56.230 No. PPM No. PPM 39 50.103 66 38.248 40 50.023 67 35.592 41 48.062 68.353.390 42 47.789 69 34.437 43.471.713 70 33.458 44 46.559 71.33.343 45 46.510 72 33.098 46 45.172 73.2.81347 45.074 74.732.62.148 44.22675 32.270 49 43.673 76 32.188 50 43.846 77 32.112 51 40.462 78 32.038 52 40.374 79.731.86 53 38.546 80 31.793 54 38.546 81 30.884 55 38.211 62 30.790 56 38.152 83.330.382 57 37.973 84 29.834 58.37.150 85 28.821 59 37.059 86.828.728 60 37.014 87 28.470 61 36.940 88 27.9962 38.732 89 27.883 63 38.853 90 27.188 64

| No. | PPM |
|--------------------------------------|-------------|
| 9.3 | 24. 816 |
| 9.4 | 24. 715 |
| 9.5 | 24. 634 |
| 9.6 | 24. 636 |
| 9.7 | 23. 963 |
| 9.8 | 22. 775 |
| 9.9 | 21. 819 |
| 10.0 | 21. 725 |
| 10.1 | 21. 625 |
| 10.2 | 21. 373 |
| 10.3 | 21. 303 |
| 10.4 | 19. 830 |
| 10.5 | 19. 597 |
| 10.6 | 19. 317 |
| 10.7 | 19. 047 |
| 10.8 | 18. 632 |
| 10.9 | 18. 342 |
| 11.0 | 18. 253 |
| 11.1 | 18. 199 |
| 11.2 | 18. 101 |
| 11.3 | 17. 832 |
| 11.4 | 16. 845 |
| 11.5 | 16. 617 |
| 11.6 | 14. 645 |
| 11.7 | 14. 527 |
| 11.8 | 0. 337 |
| 36.558 91 26.092 65 38.349 92 25.401 | 11.9 0. 002 |

[0021] It kneaded and adjusted using 3 roll mills in the presentation ratio (a numeric value shows the weight section) as shown in application examples 1-5 and example of comparison 1 table 1, and the resin constituent for printing ink was obtained. And the ink performance evaluation of this constituent was performed.

[0022] The ink performance-evaluation approach hardenability (setting time): Stick ***** art paper by pressure with RI circuit tester, and find the irradiation time (second) which that ink stops adhering took as the setting time, after carrying out drawdown of the ink 0.6g to carton paper using RI circuit tester (Akira Seisakusho Make) and irradiating ultraviolet rays from the distance of 10cm with 80 W/cm and a high-pressure mercury lamp promptly.

Gloss of original ink and emulsification ink: Carry out macroscopic observation and evaluate the gloss (original ink gloss) of the print after hardening obtained above.

[0023] Moreover, after drawing off water make ink 0.6g and dampening water emulsify with RI circuit tester, drawdown is carried out to carton paper, it hardens on the same conditions as the time of measurement of original ink gloss, the gloss of the printing side after hardening is made into the gloss of emulsification ink, it observes similarly with the naked eye, and the following criteria estimate.

O : It is very fitness (a printing side is smooth and it is dramatically glossy).

O : Fitness (gloss is in a printing side)

** : Medium [of O and x] x : Defect (there is no gloss in a printing side and reliance does not reflect light in it, either)

[0024]

Misting : 1200 revolutions of rolls to which paper was put and ink adhered before the roll of an

inkometer are carried out, the misting of the ink is carried out, the condition of the ink which dispersed in space is observed with the naked eye, and the following criteria estimate.

O : Few (an activity — suitable)

x : Many (an activity — unsuitable)

Detergency : The detergency by the kerosene of the roll of the inkometer to which ink adhered is evaluated.

Bronzing: After carrying out drawdown to carton paper using RI circuit tester and leaving it at a room temperature for 1 hour, on the same conditions as a hardenability trial, ultraviolet rays are irradiated for 0.5 seconds, stiffen them, observe with the naked eye, and the following criteria estimate.

O : It compares with the sample which carried out drawdown direct posture, and is equivalent color tone x : Separation of a pigment and a vehicle is seen and the reflected light presents gold.

[0025]

table 1 [] An example The example of a comparison 1 2 3 4 5 1 Two products A 40 30 50 35 45 Product B 5 5 5 KAYARAD R-114 + 14035 ** FM-300 + 2 29 29 29 T-1420 + 3 34 33 TMPTA + 4 19 19 IRUGA cure -907+5 6 68 6 6 6 SKAYACURE DETX + 6 1 11 1 111 carmine 6B + 7 2424 2424 24 24 The 24 setting times (second) 0.4 0.3 0.4 0.50.4 0.3 0.3 Hara ink gloss O O O O O O O emulsification ink gloss O O O O O == ** misting O O O O O x x detergency Good Good fitness Good Defect Defect BURON zinc O O O O O x x [0026] Note +1 KAYARAD R-114 : Epicost 828 made from oil-ized Shell Epoxy Acrylic ester ghost.

+2 KAYARAD FM-300: -- the tetra-ethoxy dicyrivate of bisphenol A, and the Nippon Kayaku Co., Ltd. make -- +3 KAYARAD T-1420: dimethylolpropenetracrylate Nippon Kayaku Co., Ltd. make -- +4 KAYARAD TMPTA: trimethylolpropane tricrylate and the Nippon Kayaku Co., Ltd. make -- +5 IRUGA cure -907: The Ciba-Geigy make and photopolymerization initiator.

+6 KAYACURE DETX: The Nippon Kayaku Co., Ltd. make, photopolymerization initiator.

+7 Carmine 6B: the charge of an azo system rosy face.

[0027] The resin constituent of this invention is excellent in gloss and printabilities (a misting, detergency, bronzing, etc.) so that clearly from a table.

[0028]

[Effect of the Invention] The photoresist oligomer of this invention has the advantage which was excellent in points, such as gloss of the obtained printing ink, pigment dispersibility, and a printability, as compared with conventional solvent mold printing ink, when it is applicable to a wide range application and is especially used as a binder for printing ink by using the photoresist.

[Translation done.]